Low melting molecular complexes. Part VII[*1]. 2,3-, 2,5- and 3,4-hexanediones and their molecular complexes with chloroform.

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Dedicated to the memory of Prof. O.V.Shishkin, a colleague and a friend.

Abstract

Crystals of three isomeric 2,3-, 2,5- and 3,4-hexanediones **1**-**3** and of molecular complexes (1:2) of **2** and **3** with chloroform (**4** and **5**) were grown by *in situ* cryocrystallisation and characterized by single crystal X-ray crystallography. The intermolecular interactions and packing motifs were examined using the analysis of pairwise-energies of intermolecular interactions. The method has revealed the importance of carbonyl…carbonyl interactions in the structures **1**, **3** and **4** and the relatively weaker halogen bonds in the structures **4** and **5**.

Keywords

Pairwise energy calculations, Co-crystals, Crystal structure, Hexanedione, Intermolecular interactions.

Introduction

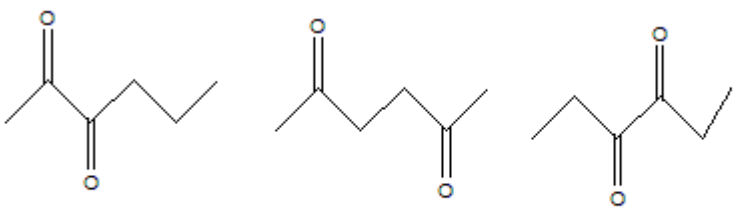
While the importance of "classical" hydrogen bonds for crystal packing is unquestionable nowadays [2], the situation with weaker interactions is more complex in spite of countless studies. Weak interactions in molecular crystals are still a hot topic for discussion among the specialists in crystal engineering and structural pharmacology. A vivid example of significance of the subject is a recent rather emotional discussion in the IUCr Journal [3]. This discussion attracts additional attention to the fundamental problem of identification of the forces, holding the molecular crystals together. Gradually it became evident that "classical" approach to description of intermolecular interactions (and therefore of the packing motifs), based on the analysis of geometry of short intermolecular contacts only, is not entirely satisfactory.

[*] Part VI see ref [XXX]

Several methods have been suggested to overcome the limitations of such geometrical analysis of weak intermolecular interactions [4]. The calculations of energies of intermolecular interactions in actual crystal structures became popular recently with rapid advances in computing power and developments in the less computationally intensive DFT methods. The basics of this method were formulated by Zorky [5] and developed further by Gavezzotti [6]. Shishkin and co-authors applied modern *ab initio* and DFT calculations to a similar energy method and suggested the vector analysis of packing motifs which helped to discover some unexpected features of molecular packing in the crystals of a wide variety of compounds [7].

In the last few years we reported the application of this approach for analysis of intermolecular interactions and packing motifs in crystals of low-melting molecular complexes (LMMC) of several common solvents (see [1]). Both components of these LMMC are liquids under ambient conditions and a non-conventional *in situ* crystallisation technique was used to obtain the crystals. Such systems, in spite of their deceptive simplicity, are interesting models for probing various weak intermolecular interactions. Moreover, being usually composed out of small molecules with a limited number of atoms and therefore relatively few intermolecular contacts, the LMMC are relatively straightforward for energy calculations and analyses.

Here we report the crystallisation and structure determination of three isomeric 2,3-, 2,5- and 3,4-hexanediones **1**-**3** and of molecular complexes (1:2 co-crystals) of **2** and **3** with chloroform (**CF**) (**4** and **5** respectively, Scheme 1). It was interesting to find out if small changes in the position of ketone group affect the pattern of intermolecular interactions and co-crystallisation ability of these diketones. In spite of all our efforts we did not manage to obtain LMMC of 2,3-hexanedione **1** with **CF**; all our co-crystallisation attempts resulted in formation of the crystals of either **1** or **CF**. We also applied the pairwise energy calculations method to analyse the intermolecular interactions and packing motifs in crystals of **1**-**5**.



1 **2** **3**

2 x Cl_3CH **4**

3 x Cl_3CH **5**

Scheme 1.

Experimental Part

Crystallisation/Single Crystal X-ray Crystallography

All chemicals were obtained from commercial sources (Aldrich, Sigma) and used without further purification. Details of the applied technique of *in situ* cryocrystallisation of low-melting compounds are described elsewhere [[8]]. A small amount of the compound (or a mixture of the compounds in the case of co-crystals) was sealed in a borosilicate glass capillary of 0.3 mm diameter and mounted on a Bruker SMART 6000 (for compounds **1**-**4** using a special attachment [[9]] which keeps the capillary in co-axial position with the stream of cold gas during the data collection) or an Agilent XCalibur diffractometer (for compound **5**; for both instruments: MoKα-radiation, λ = 0.71073Å, fine-focus sealed tube, graphite monochromator, ω-scan). Then the capillary was slowly cooled to well below the melting points of each component. If the polycrystalline material did not form then shock cooling was applied. The polycrystalline sample obtained was warmed up and partially melted until only few seeds remained at the top of the capillary and crystal growth then took place. The temperatures for the crystal growth of compounds **1**-**5** were 234.0, 267.5, 262.0, 209.5 and 205.0K respectively. When a crystal of acceptable quality was obtained, the temperature was slowly lowered by 10-20K and data were collected. The temperature on the samples has been maintained and controlled by Cryostream (Oxford Cryosystems) open-flow nitrogen cryostates. The structures were solved by direct method and refined by full-matrix least squares on F^2 for all data using Olex2 [[10]] and SHELXTL [[11]] software. All non-hydrogen atoms were refined in anisotropic approximation, hydrogen atoms were placed into the calculated positions in the structures **4** and **5** and refined in riding mode, while in the structures of **1**-**3** H atoms were refined isotropically. The crystal data and parameters of the refinements are listed in Tabl. **1**. Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-1400574-1400578.

Table 1. *Crystal data and structure refinement for compounds **1-5**.*

Compound	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_6H_{10}O_2$			$C_6H_{10}O_2$ x 2 $CHCl_3$	

Melting point/ K	235	268	263	213-214	208-210
Formula weight	114.14			352.88	
Temperature/K	220.0	250.0	250.0	200	180.0
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	C2/c	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a/Å	35.634(7)	9.4850(19)	9.7006(19)	6.4687(13)	8.1639(5)
b/Å	6.7834(14)	4.6016(9)	6.6776(13)	8.0745(16)	5.9870(3)
c/Å	5.4895(11)	8.0980(16)	5.3660(11)	15.025(3)	16.3292(10)
β/°	91.29(3)	104.35(3)	103.42(3)	98.37(3)	104.181(6)
Volume/$Å^3$	1326.6(5)	342.42(12)	338.10(12)	776.4(3)	773.81(7)
Z	8	2	2	2	2
$\rho_{calc}g/cm^3$	1.143	1.107	1.121	1.509	1.514
μ/mm^{-1}	0.085	0.082	0.083	1.090	1.094
F(000)	496.0	124.0	124.0	356.0	356.0
Reflections collected	4671	2377	2268	6012	8592
Independent reflections, R_{int}, R_{sigma}	1251, 0.0381, 0.0359	737, 0.0276, 0.0248	690, 0.0486, 0.0500	1682, 0.0256, 0.0262	2270, 0.0597, 0.0409
Data/restraints/parameters	1251/21/113	737/0/58	690/4/57	1682/0/86	2270/0/78
Goodness-of-fit on F^2	1.064	1.048	1.188	1.105	1.100
Final R_1 indexes [I≥2σ (I)]	0.0575	0.0595	0.0998	0.0377	0.0462
Final wR_2 indexes [all data]	0.1749	0.2182	0.3107	0.0974	0.1265
Largest diff. peak/hole / e $Å^{-3}$	0.14/-0.15	0.14/-0.12	0.56/-0.38	0.34/-0.32	0.65/-0.48

Calculations

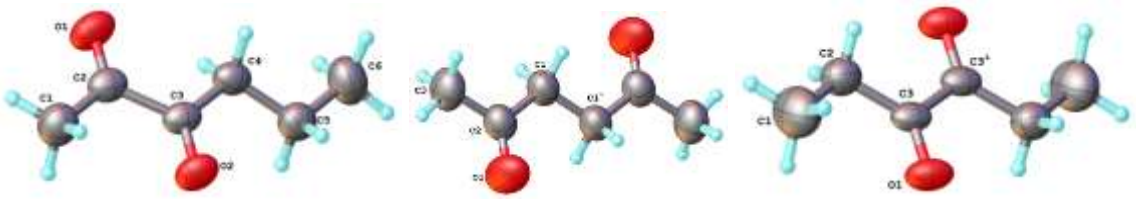
Input files of the starting geometries for single-point energy calculations were generated from the crystal structures of **1-5** using Mercury[12] software. The hydrogens in the starting geometries were normalized in all cases to neutronographic values[13]. Energies of intermolecular interactions were obtained at the computationally-intensive and robust Møller-Plesset wavefunction MP2[14] with the large basis set 6-311G(d,p)[15] using the Gaussian09 package[16].

Results and Discussion

*Structures of pure diketones **1-3**.*

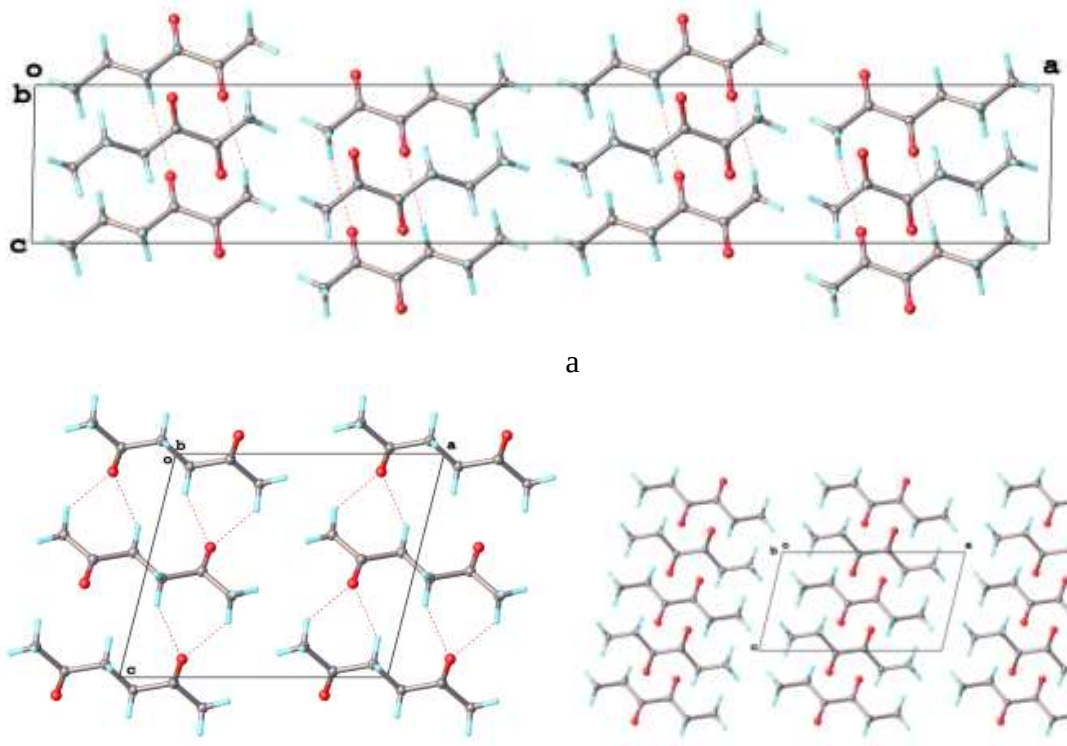
Molecular structures of pure compounds **1**-**3** are shown in Fig.1. Molecule **1** occupies a general position in crystal while molecules **2** and **3** are positioned in the centres of symmetry, which are located in the middles of the central C-C bonds. The molecules **2** and **3** are planar while the molecule **1** is slightly nonplanar with the O2C3C4C5 torsion angle of 13.8(4)° and the terminal atom C6 deviating from the plane of two carbonyl groups by 0.30Å. The geometrical parameters of the molecules are of the expected values. The longest C-C bonds are those between the carbonyl groups in molecules **1** and **3** (1.543(3) and 1.538(3)Å

respectively) and are close to those found in two reported previously linear alkyl *vic*-diones [17].



a b c

*Fig.1 Molecular structures and labelling scheme for compounds **1** (a), **2** (b) and **3** (c). The thermal ellipsoids are shown at 50% level.*



a

b c

*Fig.2 Packing of molecules **1** (a), **2** (b) and **3** (c).*

The packing of molecules **1-3** in crystals is characterized by layered arrangement of the molecules (Fig.2). The layers are in (011) planes. However, the internal architectures of these planar layers are different. The molecules in layers in all three structures are arranged in herring-bone pattern, however in structure **2,** where the carbonyl groups are not vicinal, the adjacent molecules are more inclined relatively to each other (Fig.3). As expected, short C-H…O contacts exist in all three structures and their parameters are listed in Tabl. 2. A

"classical" analysis of their geometry, based on the parameters of intermolecular contacts, suggests that molecules in layers in structures **1** and **3** are linked by double C-H…O contacts into chains, as shown in Fig.3a and 3c. Molecules in the crystal **2** are also linked by C-H…O interactions and these contacts are shorter but less linear (see Tabl.2) and forming a 2D-network. But what holds the chains of molecules together in the structures of vicinal diketones **1** and **3**? In both structures the second shortest contact exists between C and O atoms of carbonyl groups of adjacent molecules indicating carbonyl…carbonyl interactions. Such intermolecular interactions are rather uncommon but they have been observed before and summarised by Allen *et al.* [18]. On the basis of the geometrical analysis only it is impossible to conclude if in the structure **1** and **3** the double direction-specific weak hydrogen bonds C-H…O are stronger than the single carbonyl-carbonyl interaction. In order to estimate the relative importance of C-H…O and C=O…C=O interactions in the studied compounds the method of pairwise energy calculations was carried out here.

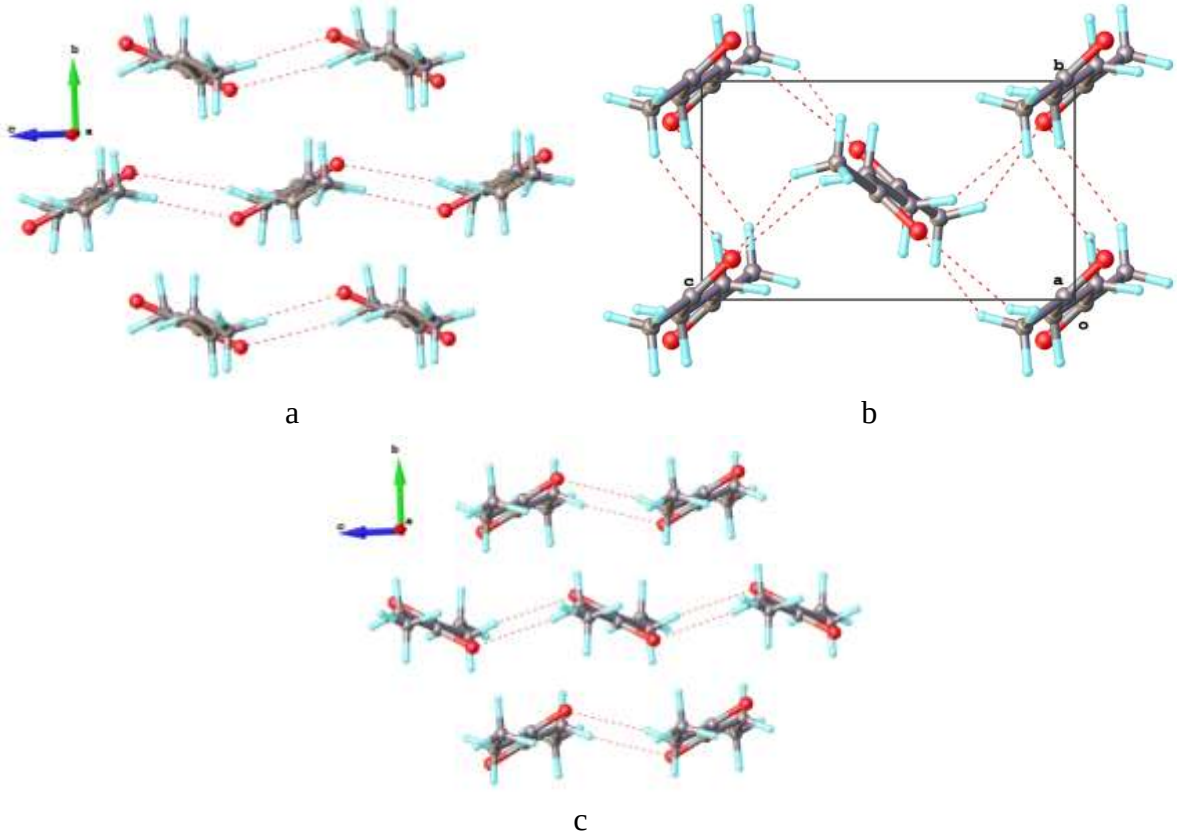


*Fig.3 Arrangement of molecules in layers in crystals of **1** (a), **2** (b) and **3** (c) (view is perpendicular to the plane of layer). Short intermolecular contacts are shown in red dotted lines*

Tabl.2 *Parameters of short C-H…O contacts in the structures **1-3***

Structure **1**						
D	**H**	**A**	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/°**
C1	H1C	O1[1]	0.987(15)	2.802(18)	3.760(4)	164(3)
C5	H5A	O2[2]	0.980(16)	2.92(3)	3.563(3)	124(2)
Structure **2**						
C1	H1A	O1[3]	0.91(3)	2.70(3)	3.423(3)	137(2)
C3	H3A	O1[3]	0.91(4)	2.78(4)	3.463(4)	133(3)
Structure **3**						
C2	H2B	O1[4]	0.91(3)	2.89(3)	3.784(4)	166(4)

[1](+x,+y,1+z); [2](+x,-y,-1/2+z); [3](1+x,1/2-y,1/2+z); [4](1+x,+y,-1+z)

The pairwise energies of intermolecular interactions in the structures **1-5** are listed in Tabl.3. The values, obtained for structures **1** and **3** are quite remarkable: the strongest interactions correspond not to C-H..O but to carbonyl…carbonyl contacts and therefore the chains in structures **1** and **3** represent secondary motif and should not be regarded as a primary building block of the structure. Thus the description of molecular patterns for **1** and **3**, based on geometrical parameters of shortest intermolecular contacts, is not in agreement with the energy calculations. There is no ambiguity in the description of the molecular packing in the structure **2**: both analyses of intermolecular contact geometries and energy calculations show that the double C-H…O contacts are the strongest interactions and distributed uniformly within the layer. The energies of intermolecular interactions between the molecules of adjacent layers is much smaller (less than 1 kcal/mol) than those between molecules within the same layer for all structures **1-3** so these structures rightfully can be defined as layered.

Table 3. *Energies of Strongest Pairwise Intermolecular Interactions and Parameters of Corresponding Intermolecular Contacts in the structures of pure hexanediones **1 - 3**.*

1:

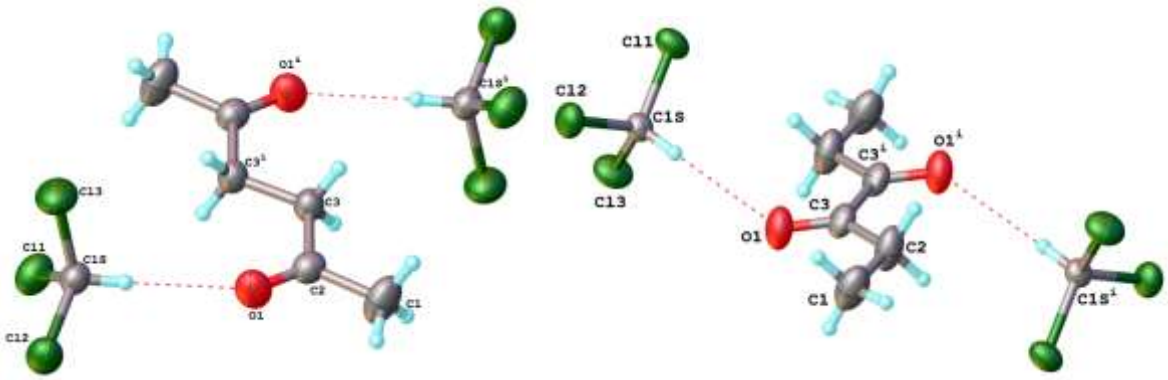
Mol 1	Mol 2 (sym.operation)	E_{int} (kcal/mol)	Contacts	Distance (Å)
2,3-Hexanedione, **1**				
x,y,z	x, 1-y, -0.5+z x, 1-y, 0.5+z	-5.37	O1…C2 H4b…O2	3.101 2.931
x,y,z	x, y, -1+z x, y, 1+z	-4.21	O1…H1c H4a…O2	2.715 2.683
x,y,z	x, -y, 0.5+z x, -y, -0.5+z	-5.79	O2…C3 H5a…H6a	3.084 2.345
x,y,z	0.5-x, 0.5-y, 1-z	-2.63	O1…H1a	2.908

			H1a…H1a	2.445
2,5-Hexanedione, **2**				
x,y,z	-x,2-y,1-z (x,1+y,z)*	-4.19	H1b…H1b H3c…O1*	2.016 2.771
x,y,z	x,0.5-y, 0.5+z	-5.97	H1a…O1 H3a…O1	2.574 2.668
x,y,z	1-x, 1-y, 1-z	-1.57	H3b…H3b	2.351
3,4-Hexanedione, **3**				
x,y,z	x,y,-1+z	-4.11	H2b…O1	2.717
x,y,z; 1-x,1-y,1-z	x,0.5-y,-0.5+z; 1-x,-0.5+y,0.5-z	-6.04	H2a…C3 O1…C3 O1…H2b	2.892 2.983 2.720

There are several possible reasons for such difference in architecture of the layers. The adjacent position of carbonyl groups in the molecules **1** and **3** make carbonyl-carbonyl interactions favourable. The different positions of carbonyl groups in the hexane backbone may alter the mutual positions of the molecules due to steric reasons. The hydrogen atoms of the ethylene link between the carbonyl groups in the structure **2**, may have less electron density thus favour the C-H…O interactions.

*Molecular structures of co-crystals **4** and **5**.*

The structures of molecular complexes of **2** and **3** with chloroform (co-crystals **4** and **5** respectively) are shown in Fig.4. In both co-crystals the hexanedione component occupies a special position in the centre of symmetry such as found in the structures **2** and **3** of pure compounds.



a b

*Fig.4. Molecular structures and labelling scheme for compounds **4** (a), and **5** (b).*

The components of co-crystals **4** and **5** are linked together by Cl_3CH…O contacts which are usual for LMMC of **CF** with ketones [19]. Both compounds show additional Cl…O contacts, which apparently combine the components into the chains of heterodimers (Fig.5a and 5b). Similar heterodimers were observed earlier in the structure of LMMC of cyclobutanone with **CF** but were not found in the corresponding LMMC with cyclohexanone and cyclopentanone [20]. Both structures **4** and **5** also contain a number of Cl…Cl, CH…Cl and C-H…O interactions of various geometries and here the calculations of pairwise energies of intermolecular interactions provide a measure of their relative importance.

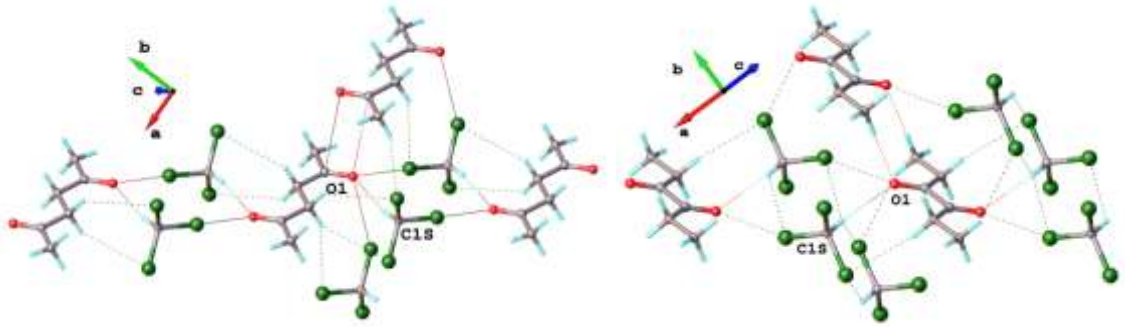


*Fig.5 Chains of heterodimers in the structures **4** (a) and **5** (b).*

The values of energies of strongest intermolecular interactions in LMMC **4** and **5** are given in Tabl. 4 and yet again the calculations reveal some unexpected features, which could not be envisaged on the basis of "classical" analysis of geometry of interatomic contacts. The strongest interactions in both structures are, indeed, those between the components of the co-crystals and the corresponding intercomponent contacts are Cl_3CH…O. However, the second strongest interactions in both cases do not correspond to the halogen bonds Cl…O. In structure **4** the carbonyl…carbonyl interactions are almost as strong as the C-H…O ones and almost twice as strong as halogen bonds Cl…O. Nevertheless the halogen bonds and C-H…Cl interactions are strong enough and the combination of all these interactions links components in all 3 directions, making **4** a real co-crystal according to Shishkin's classification [21].

Table 4. *Energies of Strongest Pairwise Intermolecular Interactions and Parameters of Corresponding Intermolecular Contacts in the structures of LMMC **4** and **5**.*

Mol1	Mol2(sym.operation)	E(kcal/mol)	Contacts	D(Å)
Co-crystal **4**				
CF(x,y,z)	2 (x,y,z)	-7.05	H1S…O1	2.194
2 (xyz)	2 (-x,2-y,1-z)	-5.24	2x(O1…C1 O1…H1c)	3.402 2.860
2 (x,y,z)	CF(1-x,1-y,1-z)	-2.58	O1…Cl1	3.351
2 (x,y,z)	CF(-x,1-y,1-z)	-2.37	O1…Cl2	3.020
CF(x,y,z)	CF(1-x,1-y,1-z)	-2.34	2x(H1s…Cl1)	3.042
2 (x,y,z)	CF(0.5+x,1.5-y,0.5+z)	-1.90	H1a…Cl3	3.084
CF(x,y,z)	CF(0.5-x,-0.5+y,0.5-z)	-1.10	Cl1…Cl3 Cl2…Cl3	3.657 3.687
CF(x,y,z)	CF(-x,1-y,1-z)	-0.71	H1S…Cl2	3.735
2 (xyz)	CF(-x,2-y,1-z)	-0.61	H1c…Cl3	3.054
Co-crystal **5**				
CF(x,y,z)	3 (x,y,z)	-5.12	H1s…O2 Cl1…H2b	2.298 2.913
3 (x,y,z)	3 (1-x,2-y,1-z)	-2.94	2xH1a…O1	3.190
3 (x,y,z)	CF(2-x,1-y,1-z)	-2.79	H1b…Cl1	3.065
CF(x,y,z)	CF(2-x,1-y,1-z)	-2.55	2xCl1…H1s	2.940
CF(x,y,z)	CF(2-x,2-y,1-z)	-2.41	2xH1s…Cl2	2.875
3 (x,y,z)	CF(2-x,2-y,1-z)	-1.91	O1…Cl2	3.092
3 (x,y,z)	CF(-0.5+x,1.5-y,0.5+z)	-1.59	H1c…Cl3	3.161
CF(x,y,z)	CF(1.5-x,0.5+y,0.5-z)	-1.02	Cl3…Cl1	3.486

It is difficult to figure out a clear "second strongest interaction" in structure **5**, where half a dozen molecular pairs show comparable pairwise energies. It should be noted that neither carbonyl…carbonyl interactions nor Cl…O halogen bonds can be considered as the second strongest ones in structure **5**. In fact, the **CF**…**CF** (C-H…Cl) interactions across the supposed hetero-dimer are stronger than Cl…O halogen bonds and it again contradicts conclusions, drawn from the 'classical' geometrical analysis of short intermolecular contacts. Like in structure **4** these interactions are propagating in 3D and thus the structure **5** may be described as a co-crystal built out of pairs of components (hetero-dimers).

Conclusions

In this paper we have described the *in situ* low-temperature crystallisation and crystal structures of three hexanediones (**1**-**3**) and of molecular complexes of **2** and **3** with chloroform (**4** and **5**). Analyses of the intermolecular interactions in these five structures were performed both by the "classical" view on the basis of geometrical parameters of shortest intermolecular contacts and by calculations of the pairwise energies of intermolecular interactions. It is shown here that, in the absence of strong hydrogen bonds, the 'classical' and pairwise energy methods yield different interpretations of some interactions. Thus, the importance of carbonyl…carbonyl interactions in the structures **1**, **3** and **4** and relative weakness of halogen bonds in the structures **4** and **5** are revealed by the energy method. Nevertheless, the robustness and repeatability of Cl_3CH…O=C "synthon" in **4** and **5** is confirmed by both methods. The energy approach provides an important insight into intermolecular bonding and that in turn makes the analysis of packing motifs more rigorous.

It should be noted that even such a short study on relatively simple molecules raises questions. For example, it is not clear why the structure **2**, in contrast to **1** and **3,** does not contain carbonyl…carbonyl interactions? Why are the carbonyl…carbonyl interactions, missing in the structure of pure 2,5-hexandione **2,** play important role in co-crystal of **2** with chloroform? Why does not 2,3-hexandione **1** (almost identical to **2** and **3**) form the co-crystals with chloroform? The structures of low-melting molecular complexes continue to be surprising.

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